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CHEMICAL SCIENCES

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CANADIAN JOURNAL OF RESEARCH

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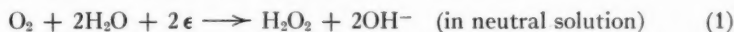
A NOTE ON THE POLAROGRAPHIC ANALYSIS OF HYDROGEN PEROXIDE¹

BY PAUL A. GIGUÈRE AND J. B. JAILLET²

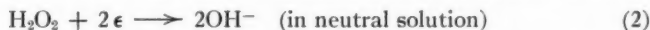
Abstract

The determination of hydrogen peroxide at concentrations higher than those normally covered in polarography was studied with various electrodes. The diffusion current was found to increase linearly with the peroxide concentration up to 0.15% with the dropping mercury electrode and up to nearly 1% with a fixed platinum microelectrode. Under these conditions the limiting current was about 10 times greater than that usually observed. Although the solutions were supersaturated with oxygen, traces of strychnine sulphate were sufficient to suppress all maxima.

In the usual practice of polarographic analysis dissolved oxygen is reduced at the cathode according to the equation:



The minute amount of hydrogen peroxide thus formed is further reduced, at higher applied e.m.f., giving rise to a second wave about equal to that for oxygen:



Recently Pellequer (5) has made a study of the conditions for maximum production of hydrogen peroxide at the dropping mercury electrode. In a previous investigation (4) the same author showed that the addition of very small quantities (of the order of 2×10^{-3} gram-equivalent per liter, i.e., 0.003%) of hydrogen peroxide to the electrolyzed solution produces a corresponding increase in the height of the second wave. This affords a method for analyzing very dilute solutions of hydrogen peroxide. Our aim in the present work was to ascertain whether the same method could be extended to somewhat more concentrated solutions and to study the behavior of solid microelectrodes under such conditions for possible application to the continuous analysis of flowing solutions.

Experimental

Most of the determinations were carried out with a Heyrovský Polarograph, Model XI (Sargent). The galvanometer had a maximum sensitivity of 0.0032 μ amp. per mm. When the diffusion currents were too large the galvanometer

¹ Manuscript received August 19, 1948.

Contribution from the Department of Chemistry, Laval University, Quebec, Que.

² Holder of a Cominco Fellowship.

was replaced by a microammeter (0–250 μ amp.) in conjunction with an Ayrton shunt. A standard Heyrovský cell was used with the dropping mercury cathode; the constant of the capillary was $1.799 \text{ mgm.}^{2/3} \text{ sec.}^{1/6}$ in 0.1 *N* potassium chloride at 1.0 v. With the solid electrodes an H-type cell, as described by Kolthoff and Lingane (2, p. 242), was used in most cases. The solid microelectrodes consisted of a few millimeters of fine platinum wire sealed at the end of soft glass tubing containing a little mercury for electrical contact. The rotating electrode was set up according to the method of Laitinen and Kolthoff (3). It was driven at 600 r.p.m. by means of a synchronous motor. The pretreatment of the solid electrodes was found to be very critical. After each analysis they were washed in concentrated nitric acid, rinsed several times in redistilled water and then heated with a Bunsen burner. If any of these treatments were omitted or their order reversed the results could not be duplicated. All analyses were carried out at constant temperature by immersing the cells in a thermostat at $25 \pm 0.1^\circ \text{C}$. The solutions were prepared by diluting some redistilled 90% hydrogen peroxide (kindly supplied by the Buffalo Electro-Chemical Co.).

Results

Preliminary work with the dropping mercury electrode disclosed one difficulty; the oxidation of mercury by hydrogen peroxide. As this reaction has already been studied, only a few tests were made to determine how it affected the polarographic analysis. With 0.1 *N* potassium chloride as supporting electrolyte there was hardly any visible sign of oxidation of the mercury anode during the electrolysis as long as the concentration of peroxide remained below 0.05%. Above that value, however, a film of oxide began forming gradually at the point where the mercury drops were falling, an indication that the reaction was taking place first at the cathode. In a 0.5% solution of hydrogen peroxide and with a relatively slow drop time (10 sec.) it was possible to observe the formation of a dull film on the surface of the growing mercury drops. The indications were that the rate of film formation increased with the applied e.m.f. Higher concentrations of electrolytes led to the following results: saturated solutions of alkali chlorides or sulphates containing up to 1% of hydrogen peroxide could be left in contact with metallic mercury for many days without any trace of oxidation of the latter. Attempts to electrolyze these solutions still resulted in film formation on the anode, although to a lesser extent than with the more dilute ones. It is noteworthy that this phenomenon did not interfere noticeably with the polarographic analysis. For instance in the determination of oxygen the same diffusion current was obtained whether the mercury anode was bright or covered with scum. On the other hand, the catalytic decomposition of hydrogen peroxide itself set a limit to the concentration of solutions that could be analyzed by this method. No matter what concentration of supporting electrolyte was used and whether or not a stabilizer was added to the solution, the limiting current at -1.2 v. ceased to be proportional to the amount of hydrogen

peroxide above 0.15% (Fig. 1). For the same reason the analysis had to be made rapidly, and on freshly prepared solutions.

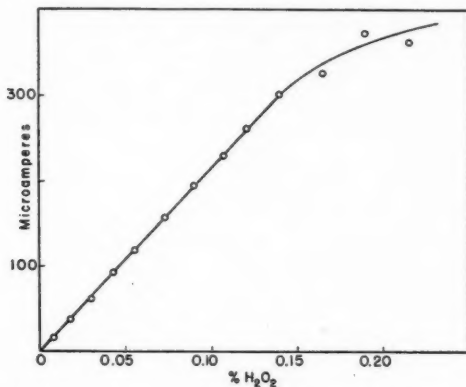


FIG. 1. Limiting current for hydrogen peroxide with a dropping mercury electrode at -1.2 v., in 0.1 *N* potassium chloride (corrected for residual current).

In order to determine the concentration of dissolved oxygen it was necessary to add a maximum suppressor, as usual. Because solutions of hydrogen peroxide are supersaturated with oxygen it was doubtful if the common surface-active substances would be effective enough. Tests showed that strychnine sulphate, 10^{-7} to 10^{-4} *M*, depending on the amount of peroxide present, was sufficient to eliminate the maximum completely. In addition to not being reduced at the dropping mercury cathode (6), strychnine sulphate is not oxidized by dilute hydrogen peroxide. Gelatin and methyl red proved less satisfactory, specially with the more concentrated solutions. The oxygen determinations were made at 0.8 v. in 0.1 *N* potassium chloride solutions containing up to 0.25% hydrogen peroxide. At first the diffusion current due to oxygen was proportional to the peroxide content up to about 0.1% ; then it leveled off gradually until at 0.2% hydrogen peroxide it reached a maximum value of 25 μ amp. At higher peroxide concentrations the behavior of the dropping mercury electrode became erratic. Comparison of the maximum value of the diffusion current thus obtained with a calibration curve of dissolved oxygen in 0.1 *N* potassium chloride extrapolated to high oxygen concentrations showed an oxygen content as high as 45 cc. per liter; the saturation value in the same conditions is 25 to 26 cc. However, this concentration is no doubt somewhat in excess of that in the bulk of the solution, and corresponds to an unstable state arising from the spontaneous decomposition of hydrogen peroxide on a fresh mercury surface in slightly alkaline medium (Equation (2) above). In some cases, nitrogen was bubbled through the solution immediately before electrolysis; the only apparent effect was to relieve momentarily the supersaturation of oxygen.

Contrary to what happens in the reduction of a charged particle, the limiting current was not affected markedly by an increase in concentration of supporting electrolyte. Hydrogen peroxide is too weakly ionized ($K_e = 2.4 \times 10^{-12}$) (1) to share appreciably in the migration current. The slight decrease shown in Fig. 2 must be attributed to a greater viscosity of the liquid, resulting in a slower diffusion rate of reducible substance.

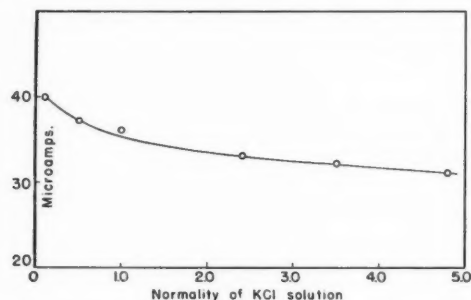


FIG. 2. Diffusion current for a 0.005 N solution of hydrogen peroxide at -1.2 v. as a function of the concentration of supporting electrolyte.

With stationary platinum electrodes, Laitinen and Kolthoff (3) were unable to observe two separate waves in the reduction of oxygen. Addition of more oxygen to the solution merely increased the limiting current at -0.2 v. and likewise in the present case, but in a much greater proportion, did the addition

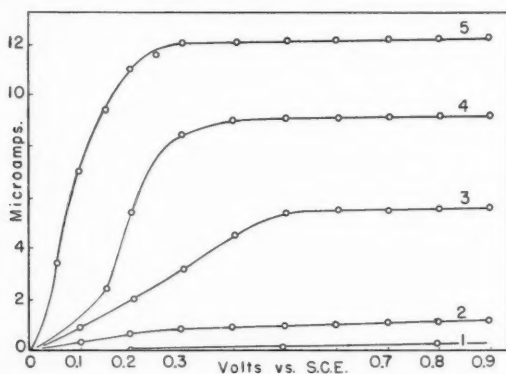


FIG. 3. Current-voltage curves with a platinum microelectrode in 0.1 N potassium chloride. (1) Residual current. (2) Solution saturated with air. (3) Solution saturated with pure oxygen gas. (4) 0.01% solution of hydrogen peroxide after bubbling nitrogen for an hour. (5) Same as (4) but without bubbling nitrogen.

of hydrogen peroxide. Also, as can be seen in Fig. 3, the wave had a tendency to be less drawn out. Because of the long time needed for reaching equilibrium, only a few current-voltage curves were measured. Most of the

determinations were done directly at -0.6 v. without progressive polarization from zero potential (Fig. 4).

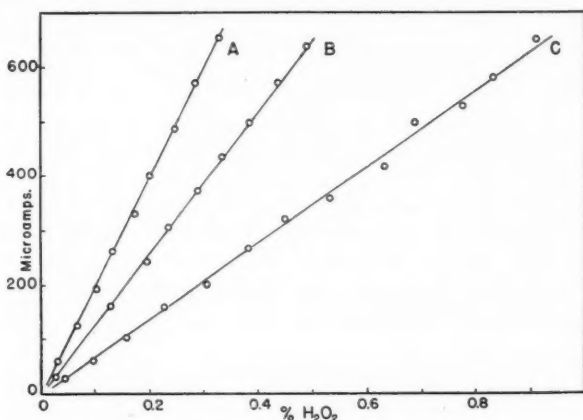


FIG. 4. Current-concentration curves with various platinum microelectrodes in saturated potassium chloride. A—2.5 mm. of B & S No. 40 wire, B—2.0 mm. of No. 28 wire, C—1.5 mm. of No. 20 wire.

As more hydrogen peroxide was added, a point was reached where the concentration of indifferent electrolyte became insufficient and the limiting current ceased to increase with the amount of reducible substance, as shown

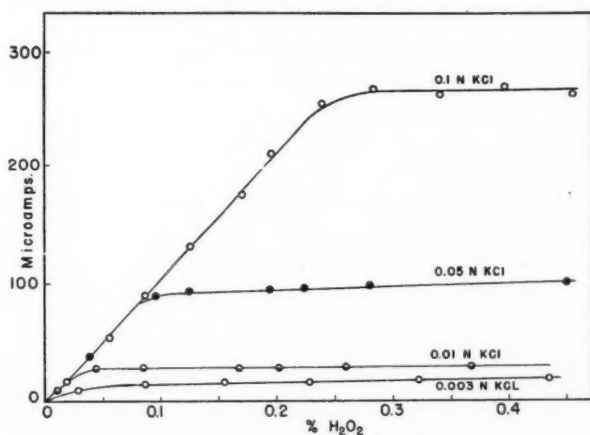


FIG. 5. Current-concentration curves with microelectrode A at various concentrations of supporting electrolyte.

in Fig. 5. This saturation value of the current was found to depend on the concentration of potassium chloride and, to a lesser extent, on the particular microelectrode used. Measurements confirmed that it varied inversely

with the electrical resistance of the cell. Thus the highest current recorded was for a solution containing about 0.9% hydrogen peroxide and saturated with potassium chloride. However, at such high concentrations the precision of the measurements diminished appreciably and fluctuations of as much as 10% were recorded in some instances.

No satisfactory results could be obtained with rotating microelectrodes of platinum or other noble metals. Addition of the faintest trace of hydrogen peroxide produced immediate changes in the shape of the current-voltage curve and increasing concentrations caused a gradual disappearance of the oxygen wave. This is not surprising in view of the fact that stirring the solution promotes further the decomposition of hydrogen peroxide so that no diffusion equilibrium can be reached. The fact that the limiting current depends both on the dissolved oxygen and the peroxide content of the solutions in the case of solid microelectrodes makes them of little value for the problem at hand.

Acknowledgment

The authors are grateful to the Consolidated Mining and Smelting Co. for the grant of a Fellowship to one of them (J. B. J.), and for permission to publish these results.

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THE SYNTHESIS OF D,L-ALANINE AND D,L-PHENYLALANINE BY WAY OF THE CORRESPONDING HYDANTOINS¹

BY ROGER GAUDRY

Abstract

D,L-Alanine was prepared in an 80% over-all yield by heating lactonitrile with ammonium carbonate to give 5-methylhydantoin, and hydrolyzing the latter with barium hydroxide into the free amino acid. D,L-Phenylalanine was likewise prepared from phenylacetaldehyde, by way of the bisulphite addition compound and 5-benzylhydantoin, followed by hydrolysis. A 40% over-all yield of the amino acid was obtained.

Introduction

Very little has been published on the synthesis of α -amino acids by way of the 5-substituted hydantoins. Many hydantoins corresponding to naturally occurring amino acids are known, but they have usually been prepared from the amino acids, instead of the amino acids being prepared from the hydantoins.

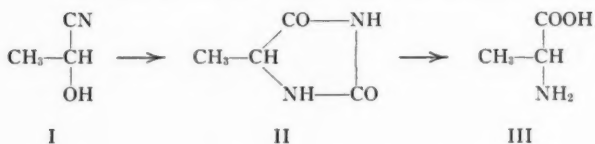
In 1934, Bucherer published two papers (1, 2) in which he describes the preparation of 5-substituted hydantoins by heating a cyanohydrin or an α -amino nitrile with ammonium carbonate. But only two of the hydantoins described by Bucherer give on hydrolysis a naturally occurring amino acid, namely 5-methylhydantoin and 5-benzylhydantoin, corresponding to alanine and phenylalanine.

The high yields obtained by us in the preparation of D,L-valine (3), D,L-methionine (5), D,L- α -amino- ϵ -hydroxycaproic acid and D,L-lysine (4) by way of the corresponding hydantoins prompted us to investigate further the preparation of D,L-alanine and D,L-phenylalanine by the Bucherer modification of the Strecker method.

It was found that D,L-alanine could be prepared most easily and economically from the commercially available lactonitrile (I) in an 80% over-all yield, in two steps: lactonitrile (I) was heated directly, in aqueous solution, with an excess of ammonium carbonate, for one hour at 55° C., to give a 90% yield of 5-methylhydantoin (II), readily recrystallized from a little water. 5-Methylhydantoin (II) was hydrolyzed in an 89 to 90% yield to D,L-alanine (III), readily obtained as the free amino acid, by heating the aqueous solution of the hydantoin under pressure with barium hydroxide, for 15 min. at 160° C., precipitating the barium with ammonium carbonate and evaporating to dryness on a boiling water bath to get rid of the excess ammonium carbonate. The method is particularly suitable for the preparation of D,L-alanine in large quantities.

¹ Manuscript received March 22, 1948.

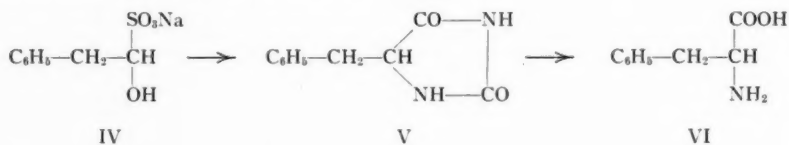
Contribution from the Department of Biochemistry of the Faculty of Medicine, Laval University, Quebec, P.Q.



Attempts were made to hydrolyze various 5-monosubstituted hydantoins with calcium hydroxide and barium hydroxide, either under reflux or in an autoclave, but the best yields were obtained by hydrolyzing hydantoins with barium hydroxide, under pressure, at 150° to 160° C. for one-quarter to one-half hour. When 5-isopropylhydantoin (3) was hydrolyzed under these conditions, D,L-valine was obtained in a 92% yield, corresponding to an over-all yield of 70% from isobutyraldehyde. But when the hydrolysis of a hydantoin was carried out at atmospheric pressure, it could usually be done satisfactorily by boiling under reflux the hydantoin with barium hydroxide for about 24 hr., the yield being slightly lower than that when the hydrolysis was made rapidly under pressure.

The hydrolysis of hydantoins by refluxing with 50 to 60% sulphuric acid was usually not satisfactory, the yields averaging only about 50% of the theoretical, and should be recommended only when the substituted part of the molecule would decompose when heated in alkaline solution.

Surprisingly, the author was unable to reproduce the 80% yield claimed by Bucherer (1) in the preparation of 5-benzylhydantoin (V) from the phenylacetaldehyde bisulphite addition compound (IV). However, with slight variation of the experimental conditions described by Bucherer, 5-benzylhydantoin (V) was prepared in a 42% yield, the best yield that could be obtained after trying many modifications in the experimental conditions. But since the preparation of the bisulphite addition compound from phenylacetaldehyde as well as the hydrolysis of the hydantoin into the free amino acid gave nearly quantitative yields, D,L-phenylalanine (VI) could be prepared in a 35 to 40% over-all yield from the aldehyde.



When the synthesis of D,L-phenylalanine was attempted by the classical Strecker method, using the experimental condition worked out by us for the preparation of D,L-valine (3), only a 10% over-all yield of amino acid was obtained.

An interesting modification of the synthesis of D,L-phenylalanine by the Bucherer method would be to use the easily available styrene oxide instead of phenyl acetaldehyde as starting material, because, according to Tiffeneau

and Fourneau (6), it is possible to prepare α -hydroxy- β -phenylpropionitrile by reacting anhydrous hydrogen cyanide and styrene oxide, in a sealed tube, at room temperature.

The reaction was tried with and without an excess of hydrogen cyanide, in solution in ethyl alcohol or in absence of solvent, at room temperature and by heating in a sealed tube to 100° to 125° C. However, all our attempts to carry out such a reaction failed completely. Whether the reaction can be made to take place under different conditions remains to be shown.

Experimental

5-Methylhydantoin (II)

Lactonitrile (71 gm., 1 mole) was added to a solution of ammonium carbonate (192 gm., 2 moles) in water (400 ml.) and the mixture was stirred at 55° C. for one hour, in a water bath. The temperature of the bath was then raised rapidly to the boiling point to decompose the excess ammonium carbonate, and the solution was filtered hot and allowed to cool. The crystalline precipitate was filtered, and the filtrate was concentrated to a small volume. On cooling, it yielded a second crop of crystals, which were recrystallized from their own weight of hot water. Yield, 102.7 gm., 90%; m.p. 149° to 151° C.* Found (Kjeldahl): N, 24.50%. Calc. for $C_4H_6O_2N_2$: N, 24.54%.

D,L-Alanine (III)

5-Methylhydantoin (57 gm., 0.5 mole) and barium hydroxide (252 gm., of the octahydrate, 0.8 mole) were added to a 2 liter beaker containing boiling water (1200 ml.), and the mixture was heated for one-half hour at 150° to 160° C. in an autoclave. After cooling, the solution was filtered from the precipitated barium carbonate, treated with ammonium carbonate (48 gm., 0.5 mole) to precipitate the barium remaining in solution, heated to the boiling point to decompose the excess ammonium carbonate, filtered again from the barium carbonate, and evaporated to dryness. The white residue was dissolved in boiling water (100 ml.), filtered hot, treated with methanol (200 ml.), and the solution was allowed to cool. The precipitate of D,L-alanine was filtered and allowed to dry. A second small crop was obtained by working up the mother liquor in the same way. Total yield, 39.6 gm. 89%. Found (Kjeldahl): N, 15.68%. Calc. for $C_3H_7O_2N$: N, 15.73%.

Phenylacetaldehyde Sodium Bisulphite Compound (IV)

Freshly fractionated phenylacetaldehyde (12 gm., 0.1 mole) and sodium bisulphite (10.4 gm., 0.1 mole) were intimately mixed in a mortar and treated with water (3 ml.). A slightly exothermic reaction took place rapidly during the mixing. Ethyl ether (25 ml.) was added to dissolve any unchanged aldehyde, and the precipitate was filtered by suction and allowed to dry. Yield, 21.8 gm., 97%.

* Melting points are uncorrected.

5-Benzylhydantoin (V)

Phenylacetaldehyde sodium bisulphite compound (67.2 gm., 0.3 mole), potassium cyanide (39 gm., 0.6 mole), and ammonium carbonate (115.2 gm., 1.2 moles) were added to a solution of ethyl alcohol (300 ml.) in water (300 ml.), and the mixture was mechanically stirred while being kept at 55° C. in a water bath for eight hours. The temperature of the bath was then rapidly raised to the boiling point to decompose the excess ammonium carbonate, and the solution was distilled *in vacuo* until only about 100 ml. of liquid remained in the flask. The mixture was cooled, and the precipitated 5-benzylhydantoin was filtered, washed on the filter with a little cold water, and immediately redissolved in boiling water (750 ml.); the solution was filtered hot and allowed to cool. The crystals were filtered and the solution was concentrated to a small volume (75 ml.) which, on cooling, yielded a second small crystalline crop. Total yield, 24 gm., 42%; m.p. 188° to 189° C. Found (Kjeldahl): N, 14.42%. Calc. for $C_{10}H_{10}O_2N_2$: N, 14.73%.

D,L-Phenylalanine (VI)

5-Benzylhydantoin (19 gm., 0.1 mole) and barium hydroxide (50.5 gm., of the octahydrate, 0.16 mole) were dissolved in boiling water (400 ml.) and the solution was heated for one-half hour in an autoclave at 150° to 160° C. After cooling down to about 50° C., the solution was filtered from the precipitated barium carbonate, and the solution was treated with ammonium carbonate (10 gm.) to precipitate the barium remaining in solution. It was then heated rapidly to the boiling point to get rid of the excess ammonium carbonate, filtered hot, and evaporated to dryness *in vacuo*. The residue was slurried with methanol (100 ml.), filtered, and allowed to dry. Yield of D,L-phenylalanine: 16.2 gm., 98%. It was recrystallized by dissolving in boiling water (300 ml.) and adding an equal volume of methanol. Found (Kjeldahl): N, 8.54%. Calc. for $C_9H_{11}O_2N$: N, 8.49%.

Acknowledgments

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THE PREPARATION OF EGG LECITHIN¹

BY R. G. SINCLAIR

Abstract

Lecithin completely free of amino nitrogen and having N/P ratios of 1.00 to 1.01 has been obtained by cooling 10% solutions of mixed egg phospholipides in absolute ethanol to -35°C . and eliminating the insoluble portions by filtration. These samples of lecithin have been considerably more unsaturated (I.N. 70 to 80) than those prepared by the cadmium chloride method of Pangborn (I.N. 55).

Introduction

The usual method of preparing pure lecithin is based upon that worked out by Bergell in 1900 (1). He made use of the observation first made by Strecker in 1868 (8) that phospholipides are precipitated from alcoholic solution by cadmium chloride and other metallic salts. Various modifications of Bergell's method have been introduced to effect a more complete removal of the cephalins. The most recent innovation is that of Pangborn (5, 6). After purification of the lecithin - cadmium chloride compound, the standard practice is to obtain the free lecithin by removing the cadmium with ammonia. The published analyses of the lecithin prepared by a great many workers show clearly that the cadmium chloride method yields a product that is wholly or almost free of amino nitrogen and thus free of cephalin. But the N/P ratios, ranging from 0.95 to 1.22, and generally about 1.05, show that the product as a rule is not *pure* lecithin.

In 1931 Sueyoshi (9) claimed that by merely cooling an alcohol solution of mixed egg phospholipides to -13°C ., the cephalins were completely removed in the alcohol-insoluble fraction, leaving pure lecithin in the alcohol. However, Bull and Frampton (2) were unable to confirm this finding. After removal of the material that was insoluble in alcohol at -15°C ., their lecithin still contained 0.106% amino nitrogen, i.e., about 6% cephalin.

Using somewhat different conditions, the author has been able to prepare by temperature-solvent fractionation samples of lecithin that are quite as pure as those prepared by the cadmium chloride method. The only striking difference between the two products is in the degree of unsaturation. The lecithin prepared by fractionation of the alcohol solution of egg phospholipides has had an iodine number of 70 to 80; that prepared by the cadmium chloride method has had an iodine number of about 55.

Experimental

The following conditions were standard throughout:

(a) All operations, so far as practicable, were carried out either in a refrigerated cabinet at $-35^{\circ} \pm 2^{\circ}\text{C}$. or in a refrigerated room at $+4^{\circ}\text{C}$. Centri-

¹ Manuscript received July 13, 1948.

Contribution from the Department of Biochemistry, Queen's University, Kingston, Ont. This work was in part supported by funds provided by the National Research Council of Canada.

fuging was done at $+4^{\circ}\text{C}$. Filtrations were carried out with sintered glass filters at -35 , $+4$, or room temperature as desired. Solvents were evaporated at $+40^{\circ}\text{C}$. or lower, under reduced pressure. Exposure to light was kept minimal.

(b) The solvents used were prepared as follows: acetone was distilled from solid potassium permanganate and then redistilled from Drierite*; ethyl alcohol was distilled from calcium oxide; its concentration was about 99%; ethyl ether was let stand in contact with sodium, then distilled, and stored in the dark at $+4^{\circ}\text{C}$.; the chloroform was Merck, U.S.P. grade, redistilled.

(c) Nitrogen and phosphorus determinations were carried out on the same sample after digestion with concentrated or fuming sulphuric acid and a mixture of copper sulphate and potassium sulphate (7). Nitrogen was determined by micro-Kjeldahl, phosphorus by the method of Fiske and Subbarow (4).

Choline was determined essentially as prescribed by Entenman and Chaikoff (3).

For amino nitrogen determination a sample was hydrolyzed by boiling for 15 to 18 hr. with 0.5 *N* hydrochloric acid in absolute methanol. After evaporation of the methanol in a stream of air, the methyl esters of the fatty acids were extracted with ethyl ether and washed well with water. The wash waters were added to the ether-insoluble residue and evaporated; thus all trace of ether and methanol was removed. The residue was again dissolved in water, filtered through asbestos to remove traces of insoluble material, and analyzed by Van Slyke's method (10).

The methyl esters of the fatty acids were recovered from the ether solution, dissolved in petroleum ether, freed from any insoluble material by centrifuging, and then dried.

Iodine numbers were determined on the intact phospholipide by Yasuda's method (11).

ISOLATION OF LECITHIN BY TEMPERATURE-SOLVENT FRACTIONATION

The starting material was a mixture of phospholipides that had been obtained from egg yolks by extracting the latter once with acetone and once with methyl alcohol, evaporating the solvents, taking up the lipides in ethyl ether, and fractionating into acetone-soluble and acetone-insoluble fractions. The latter fraction was redissolved in ethyl ether, let stand at $+4^{\circ}\text{C}$.; centrifuged free of insoluble material, and again precipitated with acetone. This mixture of phospholipides was found to contain 1.88% N, 3.86% P, 0.42% amino N, and 1.45% choline N. The calculated ratios were: N/P, 1.08; amino N/total N, 0.23; choline N/total N, 0.77. Several different fractionations were carried out but the procedure used and the results obtained in three only will be described.

* W. A. Hammond Drierite Company, Yellow Springs, Ohio.

Fractionation No. 1

Mixed phospholipide (29 gm.) was dissolved in 580 ml. of ethyl alcohol, let stand at +4° C., and filtered. The precipitate was washed twice with acetone and then dried and weighed (1a).

The filtrate was let stand overnight at -35° C. and then filtered. The precipitate was redissolved in sufficient alcohol to make a 10% solution and again let stand at -35° C. The resultant precipitate was collected on a filter, washed twice with acetone, and then dried *in vacuo* (1b).

The mother liquor from the first crop of material insoluble at -35° C. was evaporated under reduced pressure and the volume was then adjusted so that the concentration was 10%. When it was allowed to stand at -35° C. a further crop of insoluble material formed. This was collected, washed twice with acetone and dried *in vacuo* (1c).

The combined alcohol mother liquors from 1b and 1c were evaporated to dryness under reduced pressure. The residue was washed twice with acetone and dried *in vacuo* (1d).

The weight and the results of the analysis of each fraction are given in Table I. It may be seen that the C/P ratios indicated that fractions c and

TABLE I
FRACTIONATION OF ALCOHOLIC SOLUTION OF EGG PHOSPHOLIPIDES

Fraction	1a	1b	1c	1d
Solubility	Insol. at +4° C.	Insol. at -35° C.	Sol. at -35° C.	Sol. at -35° C.
Yield, gm.*	0.85	15.35	2.15	7.65
Nitrogen, %	1.52	1.86	1.79	1.90
Phosphorus, %	3.60	3.89	3.72	3.65
N/P ratio	0.94	1.07	1.06	1.15
Choline/P ratio	0.53	0.76	0.97	1.02

* The total yield was 26.0 gm. or 90% of the original.

d consisted essentially of lecithin. The N/P ratios, on the other hand, showed that the nitrogen-containing impurities in the mixed phospholipides tended to remain dissolved in alcohol at -35° C., thus contaminating the lecithin.

Fractions 1c and 1d were combined, dispersed in water to form a 5% solution, and flocculated with acetone. The material now contained 1.79% N, 3.87% P, 0.10% amino N, and 1.70% choline N. The N/P ratio was 1.02; the C/P ratio was 0.97. It is clear that the product was still not pure lecithin.

Fractionation No. 2

The procedure employed was only slightly different from that used for No. 1. Mixed phospholipides (40 gm.) were dissolved in 400 ml. of alcohol, and let stand at $+4^{\circ}\text{C}$. The precipitate that formed was removed, emulsified with water, dialyzed, dried under reduced pressure, washed twice with acetone, and dried *in vacuo* (2a).

The alcohol filtrate was let stand at -35°C . overnight and then filtered at -35°C . The filtrate was evaporated to dryness under reduced pressure. The lipid was dispersed in water, flocculated with acetone, and dried *in vacuo* (2c).

The material insoluble at -35°C . was dissolved in alcohol and an aliquot was taken to determine the concentration, which was then adjusted to 10%. The solution was let stand at -35°C . and filtered. The filtrate was evaporated and the resultant residue (2d) was dispersed in water.

The material insoluble at -35°C . was again dissolved in alcohol to form a 10% solution and the solution let stand at -35°C . The precipitate (2b) was dispersed in water. The filtrate was evaporated and the residue (2e) dispersed in water.

The solutions of 2b, 2d, and 2e were dialyzed against distilled water at $+4^{\circ}\text{C}$. for three days, then evaporated to dryness under reduced pressure and dried with acetone.

The weight and the results of the analysis of each fraction are given in Table II. It will be seen that, whereas the first fractionation at -35°C .

TABLE II
FRACTIONATION OF ALCOHOLIC SOLUTION OF EGG PHOSPHOLIPIDES

Fraction	2a	2b	2c	2d	2e
Solubility	Insol. at $+4^{\circ}\text{C}$.	Insol. at -35°C .	Sol. at -35°C .	Sol. at -35°C .	Sol. at -35°C .
Yield, gm.*	1.99	18.18	8.66	2.94	2.13
Nitrogen, %	1.43	1.91	1.75	1.90	1.79
Phosphorus, %	3.77	4.00	3.82	4.18	3.97
Amino N, %	1.09	0.26	0.09	0.00	0.00
Amino N/P	0.64	0.14	0.05	—	—
N/P ratio	0.84	1.06	1.01	1.01	1.00
Choline/P ratio	0.25	0.85	0.95	0.98	0.97
Iodine number	71.2	52.4	78.3	78.6	70.3
Methyl esters of fatty acids, %	79.1	70.8	72.3	77.3	Lost

* The total yield amounted to 33.9 gm. or 85%. The loss occurred mainly in the flocculation of the aqueous solutions with acetone.

The procedures used in obtaining the data given in this table are outlined on page 778.

resulted in an alcohol-soluble portion that contained 5% cephalin and 95% lecithin, the two "recrystallizations" of the alcohol-insoluble material yielded alcohol-soluble material that was entirely free from amino nitrogen. Since

this absence of amino nitrogen was confirmed in repeated analyses, the somewhat too low C/P ratios of 0.98 and 0.97 for fractions 2*d* and 2*e* respectively are probably due to slightly low values for the choline content. Other evidence has been published (7) that indicates that the choline method as used by us tends to give slightly too low values. We feel, therefore, that fractions 2*d* and 2*e* may be considered as reasonably pure lecithin, quite as pure as those prepared by the cadmium chloride method. It may be seen that the iodine numbers of the various fractions indicate that both the unsaturation and the nature of the nitrogenous base exert an influence on the solubility of the phosphoglycerides in alcohol.

Fractionation No. 3

In this experiment, fractions 1*c*, 1*d*, and 2*c* were dissolved in alcohol, combined, and the 3.5% solution let stand at -35°C . The resultant alcohol-soluble material, consisting of 89% of the total, was found to be quite free of amino nitrogen. The analysis of this material gave the following results: N, 1.75; P, 3.85; choline N, 1.71%; iodine number, 79.9; methyl esters of fatty acids, 73.4%. The N/P ratio was 1.01; the C/P ratio was 0.98. It has been considered to be pure lecithin.

PREPARATION OF LECITHIN BY PANGBORN'S 1941 CADMIUM CHLORIDE METHOD

For comparison with the lecithins prepared as above, a sample of lecithin was prepared by Pangborn's 1941 method (5, 6). From the same lot of mixed egg phospholipide (29.2 gm.), 5.95 gm. of a product were obtained that gave the following results on analysis: N, 1.77; P, 3.85; amino N, 0.00; choline N, 1.71%; iodine number, 54.8; methyl esters of fatty acids, 70.9%. The N/P ratio was 1.02; the C/P ratio was 0.98. This product compared favorably with those prepared and described by Pangborn (5, 6).

Since the fraction of the mixed egg phospholipides which was insoluble in alcohol at -35°C . was mostly lecithin even though the cephalin content had been enriched, it was thought possible that this alcohol-insoluble material might be used for the preparation of lecithin by Pangborn's method. Two attempts were made. In one experiment, the product contained 1.86% N, 4.00% P, and 1.69% choline N, and thus had a N/P ratio of 1.03 and C/P ratio of 0.93. In the second experiment the product contained 1.78% N, 3.76% P, and 1.58% choline N, and thus had a N/P ratio of 1.05 and a C/P ratio of 0.93. These products were clearly inferior to those prepared from the original mixed phospholipide.

Discussion

The only significant difference between the lecithins prepared by fractionation of mixed egg phospholipides in alcohol solution at -35°C . and that prepared by the usual cadmium chloride method is in the degree of unsaturation. For example, the iodine numbers of the three cephalin-free samples

of lecithin prepared by temperature fractionation were 70, 79, and 80; the iodine number of the sample prepared by Pangborn's method from the same starting material was 55. There is as well a slight difference in color. Every sample of lecithin prepared by us by Pangborn's method has been snow-white in the solid state and has given a perfectly colorless solution in alcohol or chloroform. The lecithins prepared by temperature fractionation have been almost pure white when solid; the solutions in alcohol or chloroform have had a faint yellowish tinge.

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THE VISCOSITY - MOLECULAR WEIGHT RELATION FOR POLY-*levo*-2,3-BUTANEDIYL *o*-PHTHALATE¹

By R. W. WATSON AND N. H. GRACE

Abstract

The inherent viscosities of dilute solutions of acidic polyesters of high purity have been compared with number average molecular weights accurately determined by end-group titration. For unfractionated resins with a degree of polymerization from 2 to 11 ($\bar{M}_n = 480$ to 2410) the viscosity - molecular weight relation is linear in chloroform at 25° C. Where $\ln \eta_r/c = K\bar{M}_n + \beta$, $K = 1.923 \times 10^{-6}$ and $\beta = 0.0176$. For fractionated polyesters from DP 5 to 8, $K = 1.959 \times 10^{-6}$ and $\beta = 0.0161$. For unfractionated resins with a $DP > 11$, molecular weights increase more rapidly than inherent viscosities. Above $\bar{M}_n = 14,000$ for fractionated resins linearity is resumed, and the slope increases. Several attempts have been made to explain this complex relation. Apparently the short chains remain linear, and the formation of anisotropic fibers at a DP close to 100 establishes a degree of molecular orientation in the long-chain superpolyesters. Isomerization of *levo*-diol to the diastereoisomer during polycondensation is without effect on the dilute solution viscosity of the resulting resin. Preferential degradation of the longer chains is assumed to be partially responsible for the decreasing slope from DP 11 to 65. As yet it has not been possible to assess the roles played by changes in size distribution, and variation in solvation with increasing chain length, but the data point to a curved viscosity - molecular weight relation in chloroform at 25° C.

Introduction

The original Staudinger equation has been modified by various workers to

$$\ln \eta_r/c = KmM + \beta \quad (1)$$

where η_r is the relative absolute viscosity, c is the concentration in base-moles, Km and β are constants for a given solvent and series, and M is the molecular weight (12, 15, 16, 22). This equation has been found to apply over a wide range of number average molecular weights to poly- ω -hydroxy decanoate (15), to poly- ω -hydroxy undecanoate (1), and to weight average molecular weights of poly-decamethylene adipate (12). The extent of the agreement with Equation (1) which has been obtained for a number of polymers has been ascribed by Flory and Stickney to an approximate constancy, within a given polymeric series, of the \bar{M}_w/\bar{M}_n ratio (12). Above $\bar{M}_n = 17,000$ Kraemer and Van Natta observed that the Km values, for poly- ω -hydroxy decanoate gradually increase, and interpreted this departure from linearity as evidence for a curved viscosity - molecular weight relation (15). This conclusion has been contested by Staudinger and Nuss (24).

The primary aim in the present investigation has been to test the validity of the modified Staudinger equation for a new polymeric material (28). When the inherent viscosities (10) of dilute solutions of poly-*levo*-2,3-butanediyl

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o-phthalate are compared with end-group molecular weights, excellent agreement with Equation (1) is obtained up to about $\bar{M}_n = 2400$ ($DP\ 11$). Above this range the relation becomes complex.

Experimental

Acidic polyesters of high purity, both fractionated and unfractionated, were prepared, and their number average molecular weights determined by titration. The general methods of preparation have already been described (6,7). Detailed methods are given below because of the intimate dependence of dilute solution viscosity on chain-length distribution. The terms alpha-, omega-, and super-polyesters (8) refer to apparent molecular weight ranges <5000, from 5000 to 10,000 and >10,000 respectively.

Unfractionated Polymers (Series 1)

A series of 16 unfractionated resins was obtained by direct esterification. Polyester 1 was prepared by heating 148 gm. (1 mole) of *o*-phthalic anhydride (Eastman 331) and 45 gm. (0.5 mole) of *levo*-2,3-butanediol ($n_D^{25} = 1.4318$, $\alpha_D = -13.25$) at 160° to 175° C. for 30 min. The reaction product was washed three times with boiling water (1 liter—20 min. each), dissolved in reagent chloroform, dried over neutral sodium sulphate and Drierite, filtered, and most of the solvent removed at room temperature *in vacuo*. It was further dried for 24 hr. at 73° C. to relatively constant weight *in vacuo* (*vide infra*). Polyesters 2 and 3 were prepared from the washed reaction product from 1 by heating the dry neutral resin for further periods of one and two hours, respectively, at 170° C. (nitrogen) with excess of *o*-phthalic anhydride. These resins were purified and dried as described.

Polyesters 4 and 5, and 7 to 12 inclusive, in the apparent molecular weight range from 1050 to 2410, were prepared at temperatures from 180° to 210° C. over periods varying from 5 to 15 hr., and with reactant ratios from 100% molar excess *levo*-diol through equimolarity to 100% molar excess *o*-phthalic anhydride. All these reactions were carried out under deoxygenated nitrogen, and pressures were reduced from atmospheric to 1 to 5 mm. after most of the water had been removed. The reaction products were freed from unreacted diol in three to six changes of vigorously stirred boiling water. This procedure inevitably led to some fractionation, and further loss by dispersion. To obtain carboxyl-ended chains the products were dried and further reacted for periods of one or more hours at 170° C. (carbon dioxide) with one-third their weight of *o*-phthalic anhydride. From one reaction mixture a series of samples was removed at intervals of one hour. Purification and titration showed that the carboxylation of end-groups was complete in one hour under the described conditions.

Polyester 6 was inserted in this series to determine the effect of diol isomerization during polycondensation on the solution viscosity of the resulting resin. A mixture of 17 gm. (3/16 mole) of *meso*-2,3-butanediol containing a small amount of *dextro*-2,3-butanediol ($n_D^{25} = 1.4327$, $\alpha_D = +0.14$) and 17

gm. (3/16 mole) of *levo*-2,3-butanediol ($n_D^{25} = 1.4318$, $\alpha_D = -13.25$) was reacted with 55.5 gm. (3/8 mole) of *o*-phthalic anhydride at 139° C. to 156° C. under deoxygenated nitrogen at atmospheric pressure for 12 hr., and for 5 hr. at 175° C. Thirty grams of the anhydride was added, and the reaction continued at 175° C. for a further period of three hours, after which the product was purified and dried.

Difficulties attended the drying to constant weight of resins with a degree of polymerization < 11 . At room temperature (0.2 mm.) drying in a thin layer for 10 days failed to remove solvents. After 10 days at 75° C. (0.5 mm.) the weight continued to decrease by 0.5 to 0.05 weight % per day, the actual decrease depending on the *DP*. Resins with a degree of polymerization > 15 remained solid at 75° C., and could be dried to practically constant weight in the form of extremely thin films. Although no evidence for destruction of carboxyl groups was obtained, drying at temperatures above 75° C. *in vacuo* was avoided because of the tendency of combined *o*-phthalic acid to escape. Acidic polyesters held at 180° C. (0.5 mm.) for a short period were converted to almost neutral resins through the removal of *o*-phthalic acid from the ends of the chains.

In the preparation of polyester 13, 25% excess of *levo*-2,3-butanediol was reacted with *o*-phthalic anhydride at 150° to 160° C. for 12 days under deoxygenated nitrogen at atmospheric pressure. The reaction product was converted to the acidic resin, purified, and dried to constant weight. The high flow point ($> 140^\circ$ C.) of resins with a *DP* > 20 made it impossible to remove glycol and much of the free acid in boiling water. Instead the carboxylated reaction product was poured slowly into a large excess of cold water, and boiled for 30 min. to hydrolyze anhydride. The resin was cooled, powdered, air-dried at 80° C., dissolved (50%) in chloroform, and filtered after water removal. Removal of solvent *in vacuo* at room temperature was followed by two to three hours *in vacuo* at 70° C. The polyester was then dissolved in acetone, and warm water (60° to 70° C.) added with stirring. Precipitation from acetone was repeated, and the final solution in chloroform treated as previously described.

Polyesters 14 to 16 inclusive were derived from a single reaction mixture. Approximately 246 gm. (1.66 moles) of *o*-phthalic anhydride, and 150 gm. (1.66 moles) of *levo*-2,3-butanediol were heated under deoxygenated nitrogen at 190° to 210° C. for 72 hr. at atmospheric pressure. Thirty grams of the reaction product was then removed, converted to the acidic resin, and purified (polyester 14). The original reaction was continued for a further period of three days at 200° to 210° C. at atmospheric pressure, and 50 gm. of the product removed, converted to the carboxyl-ended ester, and purified (polyester 16). Under these conditions, darkening of the reaction mixture did not become excessive, although escape of volatile products formed in side reactions and later identified did take place.

The original mixture was further heated for a period of six days at 200° to 210° C., then held for one week at 139.0° to 140.0° C., and finally reacted with an excess of the anhydride for two hours at 170° C. to give polyester 15. Chain lengths in this polyester should approach the equilibrium distribution since it has been shown in unpublished work that the side reaction effecting chain degradation is negligible at 150° C.

Fractionated Polymers (Series 2, 3 and 4)

The fractionated polyesters fall into three groups. *Series 2* comprises six fractions with end-group molecular weights ranging from 1000 to 1660. Approximately 25 gm. of a pure acidic resin, made from a reaction mixture containing 100% molar excess *o*-phthalic anhydride, was dissolved in 500 ml. of freshly distilled reagent acetone. Use of a lower concentration (2%) failed to provide efficient fractionation. Redistilled reagent petroleum ether (boiling range 30° to 60° C.) served as a precipitant. In this way the specific gravity of the mixture was kept low and successive fractions settled out rapidly (six hours), leaving a clear supernatant. For each fraction, petroleum ether was added to first turbidity at 35° C., the mixture heated under reflux to clarity at its boiling point (37° C.) and placed in a room held at $4.4^\circ \pm 1.0^\circ$ C. overnight.

Series 3, also fractionated by cooling, and including six polyesters over an apparent molecular weight range from 3420 to 8910, was prepared from a 2% acetone solution of a pure acidic resin made from an equimolar mixture at a temperature not exceeding 152° C. The product was converted to the acidic resin, purified, and partially dried before fractionation. *Series 4* was prepared in a similar manner from a superpolyester, and covered a number average molecular weight range from 9270 to 21,390. The fractionations were preparative, and were not carried to completion.

Methods of Molecular Weight Estimation

(i) Determination of Neutral Equivalents

Precision titrations were made with 0.0100 *N* aqueous or 70% methanolic sodium hydroxide for polymers below and above a *DP* of 7, respectively. Preliminary titration with 0.1 *N* aqueous alkali gave an approximate neutral equivalent. The weight of powdered resin to require between 40 and 50 ml. of 0.0100 *N* sodium hydroxide for neutralization was then dissolved in 40 ml. of freshly distilled reagent acetone. Determination of the acetone blank was made after addition of an equal quantity of freshly boiled distilled water. Use of alkaline solutions standardized at 20° C., NBS methods, burettes, and material (potassium acid phthalate), along with the application of temperature (20) and burette corrections, gave neutral equivalents which showed a maximum deviation in quadruplicate of $\pm 1\%$; for lower members of the series the deviation was usually considerably less.

(ii) *Alternative Methods*

Approximate values for the number average molecular weights of seven alpha-polyesters were obtained with a differential thermometer (17). The method of determining weight average molecular weights from melt viscosities (11) is inapplicable over wide ranges to this system since a purified resin with an average DP of 30 is a semisolid mass at 140°C .

The relation between end-group molecular weight and precipitability (γ^*), defined as the total volume-fraction of nonsolvent at end-point (1, 21), was determined for a number of omega- and super-polyesters, using freshly distilled reagent acetone as the solvent and redistilled petroleum ether as precipitant. The titrations were carried out in a room held at $21.7 \pm 0.1^\circ\text{C}$. In 10.0 ml. of acetone, 0.2000 ± 0.0001 gm. of powdered resin was dissolved, and the stoppered flask left standing in a bath held at $21.2^\circ \pm 0.04^\circ\text{C}$. for 15 min. before titration. The contents of both flask and bath were stirred magnetically, and care was taken to prevent evaporation. First turbidity points were sharp.

Measurement of Viscosity

Resin of high purity, powdered in an agate mortar, was weighed (to 0.0002 gm.) on the surface of a (medium) sintered disk, mounted in a tube extending several centimeters above and below the disk. The tube below the disk was constricted to a taper small enough to permit the tube to enter the neck of a 10 ml. volumetric flask. Several milliliters of pure chloroform was then added to the filter. When the resin had dissolved, the solution was forced under pressure into the volumetric flask, which was filled with chloroform in the same way. A small excess of chloroform was added to the flask, and the stopper inserted when evaporation had reduced the gross weight to a predetermined value. This predetermined value was calculated from the densities of the solvent and of the resin (1.228 to 1.250), the volume change on mixing ($<0.1\%$), and the appropriate concentration. A concentration of 2.002% was chosen for alpha-polyesters to give an efflux time for the solution with the lowest viscosity about 10 sec. greater than that for the pure solvent. With omega- and super-polyesters the concentration was reduced to 1.001% where necessary to keep the relative viscosity below 1.3.

The viscosities of these dilute solutions decreased with time. Pure chloroform itself is unstable, and frequent checks on the purity of this solvent were necessary. Reagent chloroform, washed several times with water, was dried over sodium sulphate and Drierite: found, b.p. 61.33°C . (762.8 mm.); $n_D^{25} = 1.4427$; $d_4^{25} = 1.4800$. Over a period of months the absolute viscosity of chloroform varied as much as 1%. After repurification at short intervals it was stored in low actinic Pyrex bottles. In this way, changes in solvent efflux time were kept within a range of ± 0.1 sec. Freshly distilled reagent acetone, used as an alternative solvent, had $n_D^{25} = 1.3567$, $d_4^{25} = 0.7845$.

The modified Ostwald has been shown to be equal in accuracy to any of the known forms of capillary viscometer (4). Two types, designated by 2

and E , were used in this investigation. Type 2 for nonviscous liquids (4) was used in one complete set of observations. The entire series was then repeated using Type E (13). The mean rate of shear in both types is slightly greater than 10^3 sec.^{-1} and in this range of shear with solutions of low concentration, the viscosity is almost independent of the rate of shear (2). Within the limits of experimental error, a proportionality constant of 1.000 for relative viscosities in the two types was verified.

The constants for these instruments, obtained by calibration with gas-free water at $25.00 \pm 0.02^\circ \text{C.}$ are given in Table VII. Type 2 was found to be somewhat more sensitive to loading errors. This viscometer was provided with square-ended capillary openings, whereas the two Type E tubes were gradually tapered to trumpet-shaped openings. Variations in the value of m with the shape of the capillary openings, as well as with the velocity in the capillary, make any calculations of the kinetic energy correction an approximation. Assuming $m = 0.56$ for Type E and $m = 1.17$ for Type 2 (3), net kinetic energy corrections are $<0.1\%$, and may be neglected. Drainage errors have been shown to be $<0.05\%$ for low viscosity data (13), and surface tension errors, absent in Type 2, are negligible in Type E . Alignment errors were avoided by the use of a plumb bob suspended in the larger arm.

All viscosity measurements were made on fresh solutions at $25.00 \pm 0.02^\circ \text{C.}$ Before transferring a solution to the viscometer, the volumetric flask was suspended in a water bath at $25.00 \pm 0.02^\circ \text{C.}$ for about 15 min. Exactly 2.5 ml. of the solution was then transferred with a pipette, which was inserted to the bottom of the larger arm. After the viscometer had reached bath temperature, the solution was forced into the efflux bulb with dried filtered air.

In view of the practice necessary for accuracy, and the observed variations in efflux times, it seemed inconsistent to attempt greater precision in visual timing than to the nearest tenth of a second. Two 0.1 sec. stop watches were used, checked against an electric timer. Variations in the efflux times of dilute polyester solutions ($c = 2.002 \text{ gm. per } 100 \text{ ml. solution}$) reported in Table II compare with those given for pure carbon tetrachloride (27). With every precaution about 10% of the determinations had to be discarded through failure to eliminate the larger particles of dust.

No corrections for differences in density between solvent and solution were applied. It has therefore been assumed but not proved in the present investigation that the solutions used in the viscosity determinations were sufficiently dilute to justify omission of the d/d_0 term in the equation $\eta_r = \nu d/\nu_0 d_0$. Following the suggestions of Wall and Cragg (10) the symbol ν_r for relative kinematic viscosity is therefore used in place of the more usual η_r . Since $\ln \nu_r/c$ was found to be approximately constant over the range of concentrations used $\ln \nu_r/c \cong [(\ln \nu_r)/c]_0$. However several workers (1, 16) have shown that $\ln \nu_r/c$ is not entirely independent of concentration. To avoid the implication of a higher degree of precision than was actually attained in these measurements, the term *inherent* viscosity recommended by Cragg for $\ln \nu_r/c$ is preferred.

Products of Side Reactions

The volatile products removed in the nitrogen stream from one reaction mixture were collected in a trap cooled by a mixture of dry ice in acetone. Butanone-2, water, the cyclic methyl ethyl ketal, and 2,3-butanediol were identified in the material retained by the trap. Butanone-2, transformed to its 2,4-dinitrophenylhydrazone, melted at 116.8° to 117.3°C. (corr.). A mixture with the derivative prepared from pure methyl ethyl ketone also melted at 116.8° to 117.3°C. (corr.). The cyclic ketal was identified by its boiling point [133.1° C. (755 mm.) corr.], by its refractive index ($n_D^{25} = 1.4030$), optical rotation ($\alpha_D^{25} = -14.57$), and camphorlike odor (18).

Isomerization of Diol

From a reaction mixture originally containing 100% molar excess of *levo*-2,3-butanediol ($n_D^{25} = 1.4318$, $\alpha_D = -13.25$), after 24 hr. at 185° to 208° C., the distillable substances were removed *in vacuo*. A small sample of the distillate (10 ml.) was redistilled without fractionation of the diols to remove water, butanone-2, and ketal. The product had $\alpha_D = -8.46$, $n_D^{25} = 1.4320$. Analysis of this distillate by a recently developed method (19) showed the presence of 35% *meso*-, 60% *levo*-, and 5% DL-2,3-butanediol.

Results

The number average molecular weights calculated from neutral equivalents and the inherent viscosities of the unfractionated polyesters are listed in Table I. The molecular weights of polyesters 1, 5, and 12 estimated ebullio-

TABLE I
UNFRACTIONATED ALPHA-, OMEGA- AND SUPER-POLYESTERS. SERIES I

Poly- ester	\bar{M}_n (end- group)	\bar{M}_n (ebullio- scopic)	γ^*	ν_r	$\ln \nu_r/c$	ν_{sp}/c	$Km \times 10^4$
1†	480	465		1.054	0.0264	0.027	12.4
2	675			1.062	0.0302	0.031	10.1
3	740			1.066	0.0321	0.033	9.8
4	1050			1.081	0.0390	0.040	8.4
5	1310			1.086	0.0414	0.043	7.2
6	1370			1.090	0.0431	0.045	7.2
7	1500			1.098	0.0468	0.049	7.2
8	1540			1.099	0.0473	0.050	7.1
9	1710			1.107	0.0505	0.053	6.8
10	1750	1350		1.109	0.0515	0.054	6.8
11	1830			1.113	0.0535	0.056	6.7
12	2410			1.135	0.0633	0.067	6.1
13	4330		0.4692	1.172	0.0794	0.086	4.4
14	5570			1.213	0.0965	0.106	4.2
15	7280		0.4158	1.113*	0.1069	0.113	3.4
16	10870		0.3873	1.277	0.1222	0.138	2.8

* Concentration = 1.001 gm. per 100 ml.; all others = 2.002 gm. per 100 ml.

† Polyester 1 was the only member of the series that was not converted to the acidic resin by reaction with excess anhydride. The agreement between end-group, viscosimetric, and ebullioscopic molecular weight determinations indicates that hydroxyl-ended chains had been removed by the washing.

scopically in chloroform show fairly good agreement with those obtained by end-group titration. Values for the precipitability (γ^*) of three of the higher members of the series (polyesters 13, 15, and 16) are plotted against reciprocal molecular weights in Fig. 1. Since the three points lie on a straight line the relation may be linear.

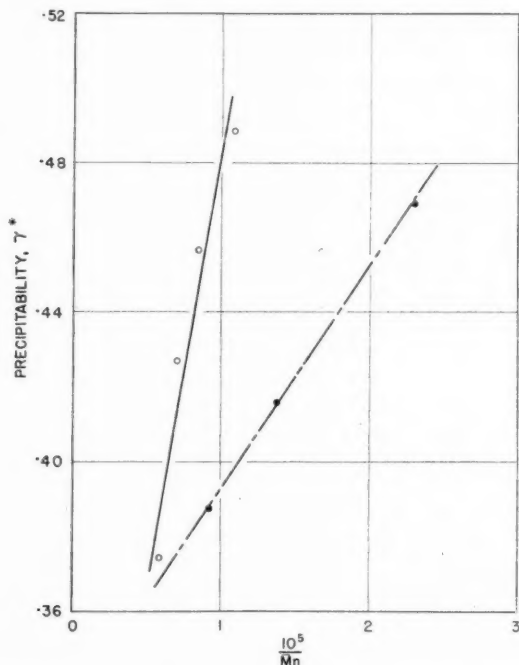


FIG. 1. Total volume-fraction of nonsolvent at end point vs. reciprocal number average molecular weight: solid circles unfractionated (Series 1); clear circles, fractionated (Series 4).

The inherent viscosities of the first 12 members of the series ($\bar{M}_n = 480$ to 2410) plotted against end-group molecular weights in Fig. 2 undoubtedly show a linear relation. Calculated by the method of least squares ($r^* = 0.998$; standard error = 0.0007) the values of K and β in the equation

$$\ln \nu_r / c = K \bar{M}_n + \beta \quad (2)$$

give $K = 1.923 \times 10^{-5}$, and $\beta = 0.0176$. The unfractionated polyesters above a degree of polymerization of about 11 ($\bar{M}_n = 2410$) possess inherent viscosities lower than those required by extrapolation of the linear relation.

* r = Correlation coefficient.

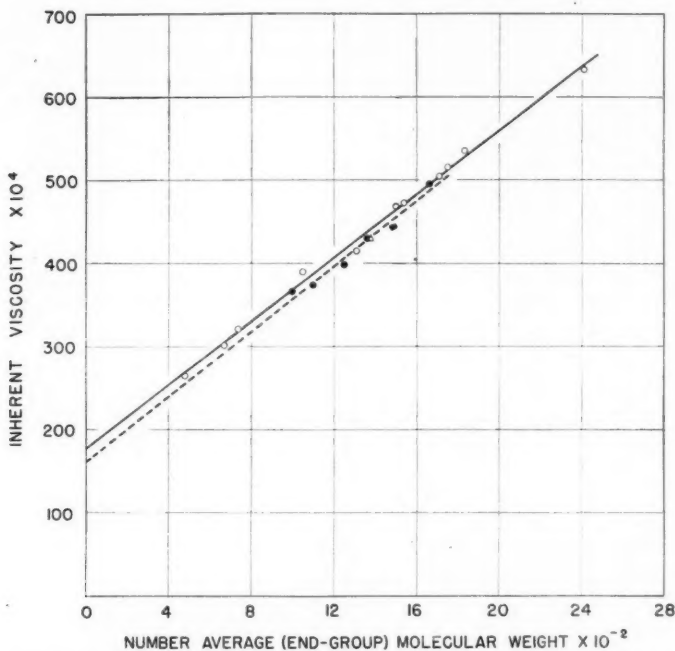


FIG. 2. Relation between inherent viscosity and end-group molecular weight of alpha-polyesters; clear circles, unfractionated (Series 1); solid circles, fractionated (Series 2); triangle, polyester 6.

This departure from linearity becomes more marked with increasing molecular weight as shown in Fig. 3.

The inherent viscosities and number average (end-group) molecular weights of the six fractionated alpha-polyesters (17 to 22) in the low-molecular range ($DP = 4$ to 8) are given in Table II. These values are plotted in Fig. 2, and show a linear relation, displaced downward from that observed for unfractionated polymers over the same range. Calculation by the method of least squares ($r = 0.985$; standard error = 0.0009) of the values of K and β in Equation (2) give $K = 1.959 \times 10^{-5}$ and $\beta = 0.0161$.

In Table III the number average (end-group) molecular weights for polyesters 23 to 28 ($\bar{M}_n = 3420$ to 8910) are listed with the corresponding inherent viscosities in chloroform. These values are plotted in Fig. 3 and also show a linear relation ($r = 0.999$).

Precipitability values (γ^*), end-group molecular weights, and inherent viscosities of the fractionated omega- and super-polyesters of Series 4 are listed in Table IV. On plotting precipitability against reciprocal molecular weight a linear relation is obtained as shown in Fig. 1. The $\ln \eta_r/c$ vs. \bar{M}_n relation is linear only for the four polyesters with the highest molecular

weights (Fig. 3). The curve departs from linearity in the vicinity of $\bar{M}_n = 14,000$ ($DP = 65$). During solvent removal *in vacuo* polyesters 33 and 34 ($\bar{M}_n = 20,060$ and $21,390$) formed brittle anisotropic structures resembling short filaments, which were best developed in polyester 34, and were not observed in any of the other superpolyesters.

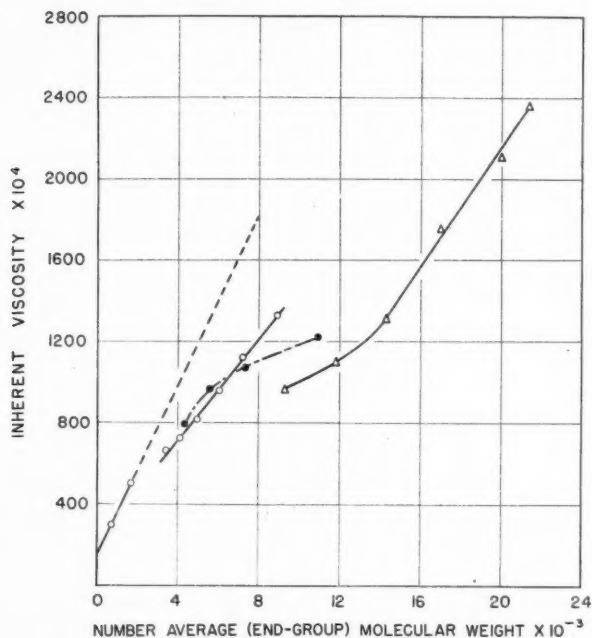


FIG. 3. Relation between end-group molecular weight and inherent viscosity: clear circles, fractionated (Series 2 and 3); solid circles, unfractionated (Series 1); triangles, fractionated (Series 4).

The conversion of *levo*-diol to the diastereoisomer under the conditions described in the experimental section led to an attempt to determine any effect isomerization might have on the dilute solution viscosity of the resulting resin. Polyester 6 ($\bar{M}_n = 1370$ —Table I and Fig. 2) prepared from a mixture of equal parts of *meso*- and *levo*-diols had the viscosity, within the limits of experimental error, calculated for a resin prepared from the pure *levo*-isomer. Substitution of optical isomers of 2,3-butanediol in polyester chains is therefore without effect on dilute solution viscosity.

The decrease with increasing chain length of the ratios of relative and inherent viscosities in acetone and chloroform of four polyesters in the range from DP 7 to 40 (Table V) is assumed to be an effect of solvation (16).

The applicability of the equation formulated for acidic polyesters from DP 2 to 11 to the viscosimetric estimation of the molecular weights of neutral resins could not be decided from the literature. Monodisperse polyoxyethylene

TABLE II
 FRACTIONATED ALPHA-POLYESTERS. SERIES 2

Poly- ester	\bar{M}_n (end group)	t_0 sec	t , sec.	$\nu_r = \frac{t}{t_0}$	$\ln \nu_r/c$	ν_{sp}/c	$Km \times 10^4$
17	1000	138.2	148.8, 148.8, 148.8, 148.9, 148.8	1.076	0.0366	0.038	8.4
18	1100	138.2	149.1, 148.9, 149.1, 148.9, 148.9	1.078	0.0374	0.039	7.8
19	1250	138.2	149.6, 149.5, 149.8, 149.8, 149.7	1.083	0.0398	0.041	7.2
20	1360	138.2	150.7, 150.6, 150.6, 150.8, 150.6	1.090	0.0431	0.045	7.3
21	1490	138.2	151.0, 151.1, 151.2, 151.1, 151.0	1.093	0.0443	0.047	6.9
22	1660	138.2	152.6, 152.6, 152.7, 152.7, 152.6	1.104	0.0496	0.052	6.9

 TABLE III
 FRACTIONATED ALPHA- AND OMEGA-POLYESTERS. SERIES 3

Polyester	\bar{M}_n (end-group)	$\ln \nu_r/c$
23	3420	0.0664
24	4130	0.0724
25	4950	0.0817
26	6040	0.0962
27	7180	0.1120
28	8910	0.1327

 TABLE IV
 FRACTIONATED OMEGA- AND SUPER-POLYESTERS. SERIES 4

Polyester	\bar{M}_n (end-group)	$\ln \nu_r/c$	γ^*	$\frac{10^5}{\bar{M}_n}$
29	9270	0.0963	0.4885	1.085
30	11810	0.1096	0.4565	0.847
31	14310	0.1310	0.4270	0.699
32	17060	0.1748	0.3742	0.586
33	20060	0.2110		
34	21390	0.2350		

 TABLE V
 RELATIVE AND INHERENT VISCOSITIES IN ACETONE AND CHLOROFORM

Poly- ester	\bar{M}_n (end- group)	Conc. = c , gm. per 100 ml. solution	$\nu_r(\text{CH}_3)_2\text{CO}$	$\nu_r\text{CHCl}_3$	$\frac{\nu_r(\text{CH}_3)_2\text{CO}}{\nu_r\text{CHCl}_3}$	$\ln \nu_r/c (\text{CH}_3)_2\text{CO}$	$\ln \nu_r/c \text{CHCl}_3$	$\ln \nu_r/c \frac{(\text{CH}_3)_2\text{CO}}{\text{CHCl}_3}$
8	1540	2.002	1.078	1.099	0.9809	0.0377	0.0473	0.7969
11	1830	2.002	1.090	1.113	0.9795	0.0430	0.0535	0.8037
12	2410	2.002	1.100	1.135	0.9692	0.0477	0.0633	0.7536
28	8910	1.001	1.091	1.142	0.9550	0.0871	0.1327	0.6561

glycol dichlorides were found to possess definitely higher solution viscosities than pure glycols of the same chain length (16). A single observation on polydecamethylene adipate showed that carboxyl- and hydroxyl-ended polyesters with similar size distributions possessed the same solution viscosity (12). The latter result is supported by the data in Table VI, which includes the molecular weights of four neutral polyesters (35-38) determined ebullioscopically in chloroform, using a differential thermometer, and viscosimetrically in the same solvent, using the equation derived for unfractionated acidic polyesters.

Discussion

An analysis of the reliability of the end-group molecular weight estimations is followed by a discussion of the significance of the viscosity data (*a*) for the short-chain alpha-polyesters, (*b*) for the omega- and super-polyesters, and (*c*) for the filamentous super-polyesters.

The agreement between end-group, ebullioscopic, and viscosimetric estimations of the apparent molecular weights up to a *DP* of about 11 (Tables I and VI) is evidence for their dependability over this range. Above $\bar{M}_n = 3000$,

TABLE VI
EFFECT OF TERMINAL GROUPS

Poly- ester	\bar{M}_n (ebullio- scopic)	Conc. = <i>c</i> , gm. per 100 ml. solution	<i>t</i> ₀ sec.	<i>t</i> , sec.	$\nu_r = \frac{t}{t_0}$	$\ln \nu_r / c$	\bar{M}_n (visco- metric)
35	810, 850	2.002	112.2	120.0, 120.0, 119.9, 120.1, 120.0	1.069	0.0334	830
36	1290 1420	2.002	112.2	122.4, 122.5, 122.5, 122.6	1.091	0.0435	1350
37	1390 1460	2.002	112.2	122.2, 122.2, 122.3, 122.1, 122.2	1.089	0.0427	1300
38	2020 2270	2.002	112.2	126.0, 126.0, 126.0, 126.0	1.123	0.0578	2080

where ebullioscopic methods are lacking in precision, self-consistency in molecular weights determined by an end-group method is not a valid criterion for their reliability. This is indicated in the long controversy over the poly- ω -hydroxy decanoates (15, 23, 24). Staudinger and Nuss found that the end-group molecular weights of these decanoates, calculated from neutral equivalents, agreed with those determined from the methoxyl content of methyl esters but were lower than the values derived from acetyl numbers. The acetyl values, however, agreed with those determined viscosimetrically. Apparently the number of hydroxyl groups had remained normal, while carboxyl groups had disappeared (24).

It is well established that a linear relation exists between precipitability (γ^*) and the reciprocal number average molecular weights of linear omega- and super-polyesters (1, 21). In this investigation a straight line relation

between γ^* and $1/\bar{M}n$ has been demonstrated for four fractionated polyesters (Fig. 1, Series 4) and the results for three unfractionated polymers are in agreement (Fig. 1, Series 1). These data indicate the reliability within the limits of experimental error of the molecular weights, calculated from neutral equivalents, from $\bar{M}n = 4330$ to 17,060 (Tables I, III, and IV).

A strictly linear relation between dilute solution viscosity and end-group molecular weight has been established over the range from DP 2 to 11. For short-chain alpha-polyesters, the lack of a method for obtaining sharp fractions makes a definitive determination of the *intrinsic* viscosity-molecular weight relation difficult. Wide deviations in the methods of preparation of the unfractionated members of Series 1 make it unlikely that any two possess the same size distribution, yet the variations in inherent viscosity produced by the differences in size distribution over this range must be slight, since the standard error of estimate for Series 1 = 0.0007. The fractionated alpha-polyesters of Series 2 are undoubtedly more homogeneous than the alpha-polyesters of the unfractionated series, and therefore should allow a closer estimation of the $[\eta]$ vs. $\bar{M}n$ relation.

TABLE VII
CONSTANTS OF OSTWALD VISCOMETERS

Type	Capillary diameter, cm.	Capillary length, cm.	Efflux time, CHCl_3 -25.00°C. $\pm 0.02^\circ \text{C.}$, sec.	Vol. of efflux bulb, ml.	Average fluid head, cm.	Efflux time, H_2O -25.00°C. $\pm 0.02^\circ \text{C.}$, sec.	Viscometer constant $K = \frac{\eta}{dt}$
2	0.0349 to 0.0351	13.5	112.2	1.006	14.1	280.2	0.003199
E ₁	0.0306 to 0.0312	13.7	138.2	1.043	17.7	346.0	0.002590
E ₂	0.0311 to 0.0313	13.5	130.6	1.037	17.8	327.1	0.002741

Since

$$\ln \nu_r/c \cong [(\ln \nu_r)/c]_0 \cong [\eta]$$

in the equation

$$[\eta]_{\text{CHCl}_3}^{25} = K' \bar{M}n^a \quad (3)$$

(for Series 1) $K' = 9.00 \times 10^{-4}$, and $a = 0.541$, and (for Series 2) $K' = 5.83 \times 10^{-4}$, and $a = 0.596$. The value of a may therefore be in the neighborhood of 0.6. In view of the uncertainty of this value, and the present uncertainty regarding the mechanisms of flow of coiled macromolecules in solution (9), no estimate of the degree of molecular coiling may be made from these data (14).

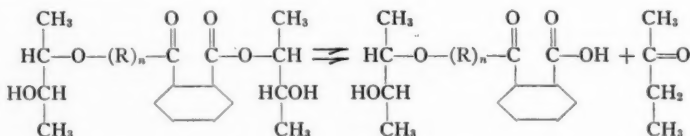
To afford comparison with the Staudinger constants (22) Km values for fractionated (Table II) and unfractionated (Table I) alpha-polyesters have been calculated from the equation

$$\nu_{sp}/c = KmM, \quad (4)$$

where c is the concentration in base-moles, Km is a constant for a given solvent and series, and M is the number average molecular weight. The recurring unit in the present polyester has a molecular weight of 220 ($C_{12}H_{12}O_4$) and $Km = \frac{v_{sp}/c \times 22}{\bar{M}_n}$. The calculated Km values gradually decrease as the

degree of polymerization increases. From DP 2 to 4 the values fall rapidly. From DP 4 to 11 the average Km is about 7.2 (Table I). Dividing this average value by the number of atoms in the basic unit gives the Staudinger constant $Keq.$ (27). In the present instance $n = 8$, so that $Keq.$ is approximately 0.9×10^{-4} , which is close to the value reported by Staudinger for paraffin hydrocarbons (0.85×10^{-4}) and somewhat lower than the constant given for ethylene glycol diesters in chloroform at $20^\circ C.$ (1.1×10^{-4}) (26).

The molecular weights of unfractionated polyesters with a $DP > 11$ increase more rapidly than inherent viscosities, and Km values decrease (Table I). The side reaction resulting in the formation of butanone-2 and the cyclic methyl ethyl ketal may contribute to this curved relation. Polyester 15 (Table I), which was held at 200° to $210^\circ C.$ six days longer than polyester 16 (see experimental section), possesses a lower end-group molecular weight as determined by titration. During the six-day period at 200° to $210^\circ C.$ volatile products, later identified as butanone-2 and the cyclic methyl ethyl ketal, continually escaped in small amounts from the reaction mixture. This observation indicates that reduction in chain length is associated with a side reaction under these conditions. Complete degradation of the chains has been established in unpublished work, and evidence links the degradation with ketonization. This result can be explained by assuming the following reaction to take place:



It has been indicated that phthalic acid is readily removed from the ends of the chains, so that the process is continuous. The cyclic ketal is formed by the reaction of butanone-2 with 2,3-butanediol. Although knowledge of the detailed effects of this depolymerization reaction on size distribution is lacking, the occurrence of this reaction offers a simple explanation, through changes in size distribution, for at least part of the decrease in the Km values of higher members of the unfractionated series.

Differences in slope and intercept persist between the linear relations based on the lower alpha-polyesters and those of the fractionated omega- and super-polyesters. Inadequate fractionation does not suffice to explain these differences, and variation in solvation with increasing chain length may play a part. The decrease in the ratios of inherent viscosities in acetone and chloroform with increasing molecular weight (Table V) indicates that solvation

may have produced some distortion of the results (25). For the differences in viscosity of equally concentrated solutions in different solvents, however, a whole series of factors must be considered. Both acetone and chloroform are good solvents for this polyester. Elucidation of the significance of solvation must await measurements at different temperatures in an intermediate solvent (e.g., benzene) (25).

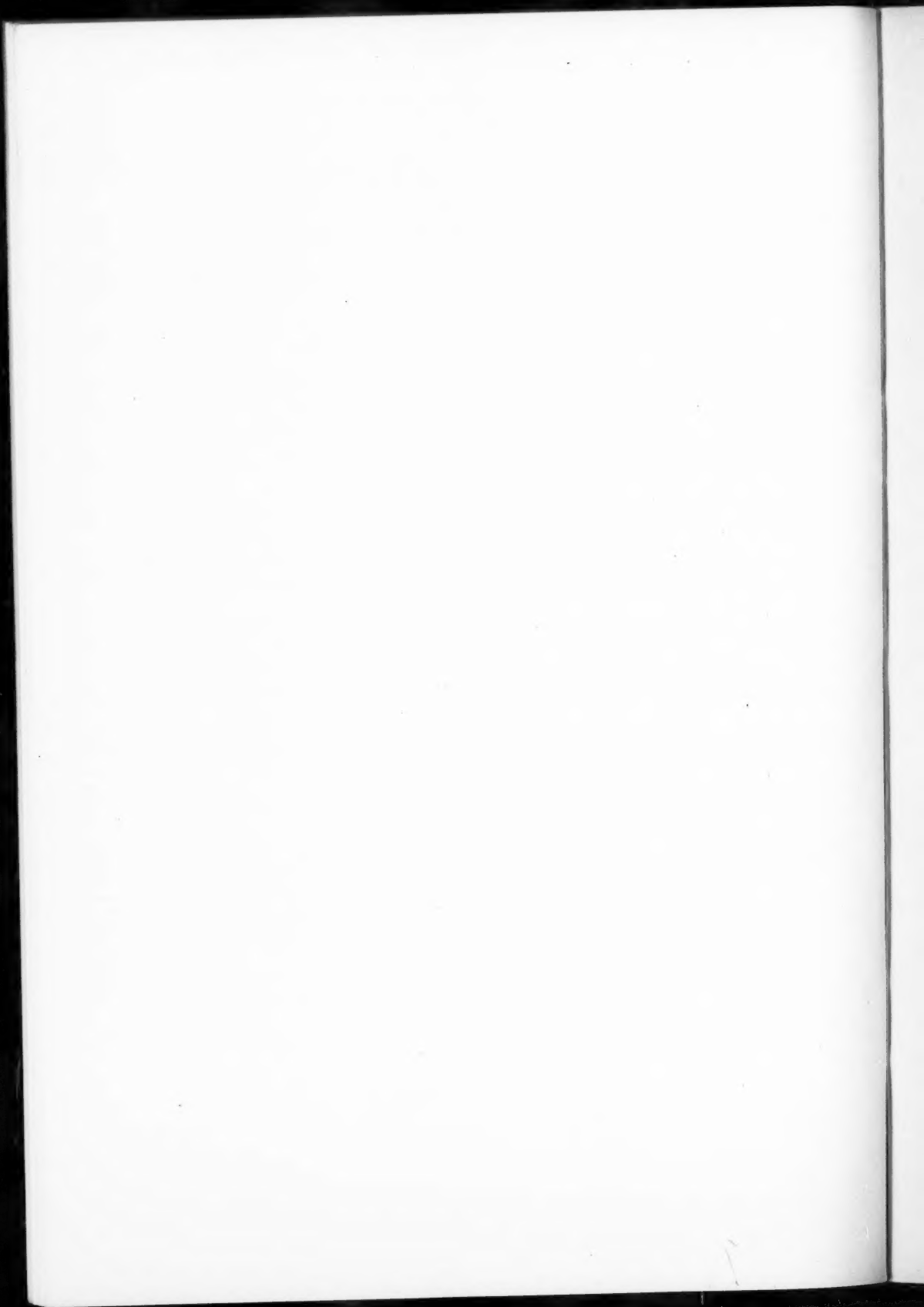
The formation of anisotropic fibers in superpolyesters at a *DP* close to 100 reveals a certain degree of order in the molecular arrangement of these long chains, even though orientation does not attain the level of crystallinity. Polyesters from glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$ and *o*-phthalic anhydride have invariably been amorphous resins, over the range of molecular weights investigated (5); and the lateral methyl groups in the 1,2 dimethyl-substituted glycol should diminish the tendency to orientation in its polyesters. Chain irregularity is further increased by isomerization of the diol during esterification.

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